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Imaging of Individual Eu Doped Y_2O_3 Sub-microspheres Using Photoluminescence Yield: An Application of Scanning Transmission X-ray Microscopy in Luminescent Materials

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Scanning transmission X-ray microscopy (STXM) employs a nano-sized X-ray beam and provides spectro-microscopic information by measuring the absolute absorption of the specimen in transmission; thus both chemical images and detailed absorption spectroscopic features of a single nanostructure (including its thickness) can be revealed [1]. STXM-Ptychography reaches a spatial resolution of 10 nm in the hard X-ray and below 5 nm in the soft X-ray [2,3]. Recently STXM using X-ray fluorescence yield (FY) and total electron yield (TEY) mode has been developed to visualize local element segregation, chemistry and conductivity variation among different crystal facets of $LiNi_{1/3}Fe_{1/3}Mn_{4/3}O_4$ micro-sized particles at the transition metal L-edges and O K-edge, which do not suffer from the sample thickness limitation because soft X-ray cannot penetrate thick samples [4]. Jacobsen et. al. have demonstrated that scanning luminescence X-ray microscopy (SLXM) can be used to form high-resolution images of ZnS based phosphor P31 microparticles and polystyrene microspheres loaded with fluorescent dye based on the visible light emission from the sample and the fluorescent dye, respectively [5]. More recently, Vaz et. al. demonstrated imaging of the magnetic domain configuration of cobalt microstructures fabricated on MgO(001) using the photoluminescence from the MgO substrate in STXM [6]. These encourage further development of STXM with the capability of photoluminescence yield (PLY) mode for studying luminescent nanomaterials. Here we demonstrate the imaging of individual Eu doped Y_2O_3 sub-microspheres using STXM based on the optical luminescence from the sub-microspheres. Furthermore, PLY-X-ray absorption near edge structures (PLY-XANES) can be isolated from individual sub-microspheres.

Eu-doped Y_2O_3 submicrospheres were prepared by homogeneous precipitation and post-annealing with $CO(NH_2)_2$, $Y(NO_3)_3$ and $Eu(NO_3)_3$ as starting materials. STXM measurement was carried out at the SM beamline of the Canadian Light Source (CLS). A 25 nm outermost-zone zone plate (CXRO, Berkeley Lab) is used and the diffraction-limited spatial resolution for this zone plate is 30 nm. As shown in Figure 1, the detector was modified to only collect the optical luminescence emitted from the sample. More details of STXM measurement and data analysis can be found elsewhere [7].

Figure 2a shows a STXM image of Eu doped Y_2O_3 submicrospheres that monitored the optical luminescence emitted from the submicrospheres when excited at 540 eV. The morphology of the sample is well resolved, showing spherical shape with diameter of about 250-500 nm. The luminescence intensity is much stronger at the center than the edge area of single submicrospheres (e.g.: as marked by green dashed circle), suggesting that the sample is solid, not a hollow structure. The STXM image is consistent

with SEM and TEM observations (not shown here). As shown in Figure 2b, O K-edge PLY-XANES of individual Eu doped Y_2O_3 submicrospheres are obtained from the dashed circles as outlined in Figure 2a, which recorded the optical luminescence from single particles as a function of incident photon energy. All PLY spectra show the same features coming from O 1s-2p transitions. It indicates that the sample is homogeneous (the PLY from the unmarked submicrospheres in Figure 2a has the same result, just not shown here). Compared to TEY and FLY (collected at SGM beamline at CLS), PLY is partially inverted due to that the energy transfer to the optical channel is less efficient at oxygen site.

In conclusion, we demonstrated the STXM imaging of Eu doped Y_2O_3 sub-microspheres using the luminescence emitted from the sample that well resolved the morphology of the sample. PLY-XANES of individual Eu doped Y_2O_3 sub-microspheres is also obtained. It encourages further development of X-ray excited optical luminescence (XEOL) mode to obtain the luminescence spectrum of single nanostructures in STXM [8]. This technique should be applicable to the characterization of a wide variety of light emitting micro- and nano-materials [9].

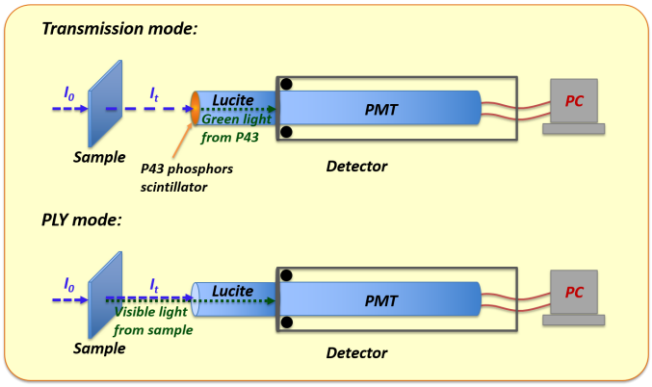

Figure 1. Schematic illustration of the detectors used in the conventional transmission mode and PLY mode. In PLY mode, the P43 phosphors scintillator was removed, therefore the luminescence from the sample can penetrate the Lucite pipe tip and reach the PMT while the transmitted X-ray (I_t) cannot.

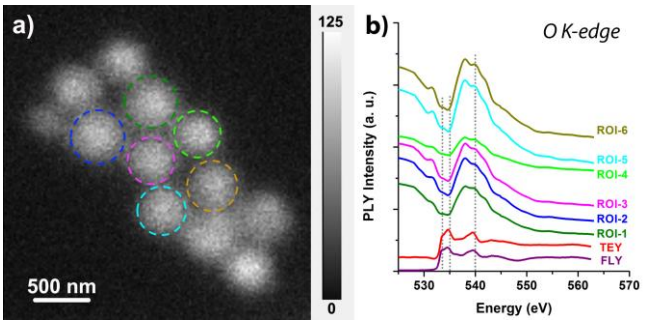

Figure 2. a) STXM image of Eu doped Y_2O_3 submicrospheres recorded at E_{ex} = 540 eV using the optical luminescence emitted from the sample. The vertical bar represents the optical luminescence intensity. b) Isolated PLY-XANES of individual submicrospheres marked in a). The color of the spectrum corresponds to the color labeled region of interest (ROI).

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